University of Victoria | Graduate Studies

Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy

of

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BSc (University of Victoria, 2012)

"Development of Mass Spectrometry Techniques for Real-Time Reaction Monitoring"

Department of Chemistry

Thursday, August 10, 2017
9:30 A.M.
David Turpin Building
Room A144

Supervisory Committee:
Dr. Scott McIndoe, Department of Chemistry, University of Victoria (Supervisor)
Dr. Natia Frank, Department of Chemistry, UVic (Member)
Dr. Dennis Hore, Department of Chemistry, Uvic (Member)
Dr. Christoph Borchers, Department of Biochemistry and Microbiology, UVic (Outside Member)

External Examiner:
Dr. Christian Hartinger, School of Chemical Sciences, University of Auckland

Chair of Oral Examination:
Dr. Graham Voss, Department of Economics, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies

Abstract

Electrospray ionization (ESI) facilitates the transfer of ions in solution into the gas-phase for analysis by mass spectrometry. The ionization process is intricate and required further investigation. To do this, a cationic ionic liquid, butyl methylimidazolium (BMIM), was paired with a counterion and mixed in various solvents. This was analyzed by ESI mass spectrometry to determine the relative response ratio between two observable aggregates. The findings assisted in the elucidation of differential surface activity of chemically distinct ions in ESI, with respect to changes in solvent. Furthermore, the results obtained suggested acetonitrile is an optimal solvent for the analysis of ions of this type due to a reduction in differential effects, whereas other common ESI solvents prove to enhance the surface activity of specific aggregate ions.

Further investigations into ESI-MS involved effects of spray head geometry relative to the inlet to the mass spectrometer. The position of the spray-head, the solvent, and additional instrumental parameters were independently adjusted during the analysis of an equimolar mixture of two different ions. It was found that these parameters have dramatic effects on the distribution of signal intensity from one ion to another, and therefore the resulting usefulness of acquired spectra. The sharp contrast in ion intensity, and even differential ion activity, with relatively minor instrument changes (such as temperature programming, gas flow rates and solvent choice) demonstrated the importance of finding the optimal spot for the ESI spray head, especially when signal intensity and a quality analysis is key.

Additional ESI-MS work involved working with an industry partner to develop selective charge-tagging reagents for the characterization of petroleum fractions by ESI-MS. A simple chemical derivatization technique was developed for in which thiols and disulfides may be selectively analyzed in a complex matrix and easily characterized. These reagents enhanced detection of thiols and disulfides solely due to the nature of the charged tag derivatization agent. The charged disulfides readily and exclusively

react with thiols in a complex matrix in a short amount of time. The synthesis of these reagents was simple and resulted in a pure and stable reagent. The efficacy of the reaction was demonstrated using on-line monitoring, while the scope and usefulness of the reaction was demonstrated in petroleum fractions.

A combination of UV-Vis spectroscopy and electrospray ionization mass spectrometry was used for real-time monitoring of Pd2(dba)3 activation with sulfonated versions of PPh3 and a Buchwald-type ligand. This provides insight into the effect of ligand and preparation conditions on activation and allows for establishment of rational activation protocols. It is expected that this reaction monitoring technique will be enhanced through the use of tandem mass spectrometry.

Finally, an experimental method of visualizing atomic orbitals was developed as a demonstration intended for first year chemistry students. This demonstration involved the examination of nodal and anti-nodal regions of Chladni figures which students could then connect to the concept of quantum mechanical parameters and their relationship to atomic orbital shape.